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Covalency reduction factors in D_{4h} symmetry and estimation of bonding parameters from magnetic data

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The expressions for covalency reduction factors for orbital moment and S.O. coupling constant in the case of a complex having D_{4h} symmetry have been derived in terms of mixing co-efficients of the ligands with the central atom (bonding parameters) and overlap integrals. So far, no explicit expressions for covalency reduction factors in an anisotropic complex have been given, only the isotropic case has been treated It is known that these anisotropic reduction factors can be obtained from magnetic anisotropy and susceptibility data. It has been shown that the expressions for anisotropic reduction factors along with the magnetic data in the case of complexes having D_{4h} symmetry provide a simple method to determine the bonding parameters even without the help of epr or hyperfine structure measurements.

Introduction

It is now well established that the orbitals of the magnetic electrons of the iron group of ions are not of pure $3d$—type and are considerably modified by their admixture with the ligand orbitals. The motions of the electrons actually participating in the bond formation in the co-ordination complexes are polycentric and not monocentric as in the case of the single atom. In other words, charge clouds of such electrons originally belonging to the central atom and surrounding ligands overlap one another resulting in a covalent type of bonding. The consequence of this will bear significantly on some of the properties of the iron group complexes Since magnetic properties and optical absorption in iron group ions are primarily dependent on the orbitals of the unfilled shell of the central metal atom, these will be modified further if the central orbitals spill over into the ligand orbitals It is for this reason that the orbital moment and the spin orbit coupling co-efficient of the central metal atom appear to be considerably reduced in the complex from their respective free ion values.

The mathematical formalism to describe the motion of the magnetic electron in the complex employs the method of LCAO-MO as developed by Van Vleck (1935). Following this method Stevens (1953) and Tinkham (1956) obtained expressions for the amount of the aforesaid reduction of the orbital moment and spin orbit coupling co-efficient in an undistorted octahedral complex, in terms of overlap integrals and co-efficients of mixing of the ligand orbitals with those of the central atom, which may be called the *bonding parameters.*

Now a regular O_h symmetry occurs only in very few complexes and it is more realistic to consider them as distorted. In fact, the magnetic anisotropy of a very large number of iron group complexes, studied in our laboratory, implies that all these complexes are distorted and such distortion will apparently manifest itself in the anisotropies in some other physical properties also. It is reasonable to assume that the covalency overlap of the central atom and ligand orbitals in distorted O_h complexes should not be treated as isotropic, since the reduction of the degeneracy of the overlapping orbitals is inherently associated with symmetry operations other than cubic. The covalency effect then must partake of the symmetry of the complex.

Expressions for magnetic susceptibility and anisotropy of almost all ions of the iron group have been already derived in this laboratory on the basis of such anisotropic covalency effect. Using these expressions anisotropic covalency reduction factors for orbital moment and S.O. coupling coefficient have also been evaluated with the help of the experimental magnetic anisotropy and susceptibility data. Unfortunately, these anisotropic values cannot be used in Stevens' and Tinkham's expressions for covalency reduction factors deduced in the case of a regular octahedron, to evaluate the bonding parameters. The purpose of this communication is to give similar expressions for square planar and tetragonally distorted octahedral complexes, and to indicate a way to evaluate the bonding parameters in these cases from magnetic anisotropy and susceptibility data. The procedure at the same time throws some light on the nature of the orbitals involved in the bond formation in these complexes.

Molecular Orbitals in a Tetragonally Distorted XY_6 Complex

We consider an octahedron distorted along the Z-axis, the central metal atom being at the origin (0, 0, 0) and the ligands at ($\pm a$, 0, 0), (0 $\pm a$, 0) and (0, 0, $\pm b$). The local co-ordinate system for describing the ligand orbitals at each ligand site is taken parallel to the central co-ordinate system XYZ. We consider the most frequent case in the iron group complexes in which the central metal atom has a partly filled $3d$-shell with no electron outside it and the ligands have all shells filled upto $2p$, with outer shells completely empty. Our interest lies in the molecular orbitals of the magnetic electrons of the central atom which were originally moving in pure $3d$-orbit in the free atom. Setting up of the molecular orbitals in a tetragonally distorted hexacoordinated complex is best achieved by considering the point group symmetry of the complex as D_{4h}. Using the group theoretical method, linear combinations of the s and p valence orbitals belonging to the six ligands are constructed in such a way that the combinations transform as the various irreducible representations of D_{4h} point group. Each of them is then admixed to the corresponding central atom $3d$-orbital which spans the same irreducible representation. The antibonding molecular orbitals (denoted by ϕ functions), thus obtained are shown below :

$$A_{1g}: \phi_{z^2} = N_{1\sigma}[d_{z^2} - \lambda_{1\sigma}\{\sigma_x(1) - \sigma_x(4) + \sigma_y(2) - \sigma_y(5)\} - \lambda_{2\sigma}\{\sigma_z(6) - \sigma_z(3)\}] \quad \ldots (1)$$

$$B_{1g}: \phi_{x^2-y^2} = N_{2\sigma}[d_{x^2-y^2} - \lambda_{3\sigma}\{\sigma_x(4) - \sigma_x(1) + \sigma_y(2) - \sigma_y(5)\}] \quad \ldots (2)$$

$$E_g: \quad \phi_{xz} = N_{1\pi}[d_{xz} - \lambda_{1\pi}\{p_z(1) - p_z(4)\} - \lambda_{2\pi}\{p_x(3) - p_x(6)\}] \quad \ldots (3)$$

$$\phi_{yz} = N_{1\pi}[d_{yz} - \lambda_{1\pi}\{p_z(2) - p_z(5)\} - \lambda_{2\pi}\{p_y(3) - p_y(6)\}] \quad \ldots (4)$$

$$B_{2g}: \phi_{xy} = N_{2\pi}[d_{xy} - \lambda_{3\pi}\{p_y(1) - p_y(4) + p_x(2) - p_x(5)\}] \quad \ldots (5)$$

Since the magnetic electrons of our interest occupy antibonding molecular orbitals, we have used negative sign before λ's (the mixing co-efficients of the various ligand combinations) in the above expressions (1)—(5). The numbers 1, 2, 3 and 4, 5, 6 appearing with the ligand orbitals σ's and p's refer to the ligands on the positive and negative X, Y, Z axes, respectively We shall consider the p's to be $2p_\pi$ only and the hybrid σ's to be made up of $2p_\sigma$ and $2s$ only. The s part of the hybrid is added to the p_σ part with such sign as to reinforce the interior lobe of the p_σ orbital. Further, the $4s$ orbital of the central metal atom also spans the A_{1g} representation of D_{4h}. But we have neglected its mixing with the d_{z^2} orbital.

Thus $$\sigma_x(1) = \sin\theta\,|\,2p_x(1)> - \cos\theta\,|\,2s(1)> \quad \ldots (6)$$

while $$\sigma_x(4) = \sin\theta\,|\,2p_x(4)> + \cos\theta\,|\,2s(4)>,\ 0 < \theta < \pi/2 \quad \ldots (7)$$

The mixing co-efficients $\lambda_{i\sigma}$'s ($i = 1, 2, 3$) depend on the admixtures of p and s in the hybrid and their relation is obtained as follows

$$\lambda_{i\sigma}\sigma_x(1) = \lambda_{i\sigma}\sin\theta\,|\,2p_x(1)> - \lambda_{i\sigma}\cos\theta\,|\,2s(1)> \quad \ldots (8)$$

$$= \lambda_{ip_\sigma}\,|\,2p_x(1)> - \lambda_{is}\,|\,2s(1)>$$

where $\lambda_{ip_\sigma} = \lambda_{i\sigma}\sin\theta$ and $\lambda_{is} = \lambda_{i\sigma}\cos\theta$; whence

$$\lambda^2_{i\sigma} = \lambda^2_{ip\sigma} + \lambda^2_{is} \quad \ldots (9)$$

The same relation (9) will be obtained if we start with any other hybrid σ orbital of the ligand instead of $\sigma_x(1)$. For directed orbital $\cos\theta \approx \sin\theta \approx 1/\sqrt{2}$ and $\lambda_{ip\sigma} \approx \lambda_{is} \approx 1/\sqrt{2}\,.\,\lambda_{i\sigma}$.

The normalizing constants N's appearing in the molecular orbitals (1)—(5) are given by

$$\frac{1}{N^2_{1\pi}} = 1 + 2(\lambda^2_{1\pi} + \lambda^2_{2\pi}) - 4(\lambda_{1\pi}S_{1\pi} + \lambda_{2\pi}S_{2\pi}) \quad (10)$$

$$\frac{1}{N^2_{2\pi}} = 1 + 4\lambda^2_{3\pi} - 8\lambda_{3\pi}S_{1\pi} \quad (11)$$

$$\frac{1}{N^2_{2\sigma}} = 1 + 4\lambda^2_{3\sigma} - 8\lambda_{3\sigma}S_{1\sigma} \quad (12)$$

$$\frac{1}{N^2_{1\sigma}} = 1 + 4\lambda^2_{1\sigma} + 2\lambda^2_{2\sigma} - 8/\sqrt{3}\,.\,(\lambda_{1\sigma}S_{1\sigma} + \lambda_{2\sigma}S_{2\sigma}) \quad (13)$$

where the overlap integrals of interest are defined by

$$S_{1\pi} = \langle p_z(2)\,|\,d_{zy}\rangle = \langle p_z(1)\,|\,d_{xz}\rangle = \langle p_x(2)\,|\,d_{xy}\rangle = \langle p_y(1)\,|\,dx_{xy}\rangle$$
$$= -\langle p_z(5)\,|\,d_{yz}\rangle = -\langle p_z(4)\,|\,d_{x2}\rangle = -\langle p_x(5)\,|\,d_{xy}\rangle = -\langle p_y(4)\,|\,d_{xy}\rangle$$

$$S_{2\pi} = \langle p_x(3)\,|\,d_{xz}\rangle = \langle p_y(3)\,|\,d_{yz}\rangle = -\langle p_x(6)\,|\,d_{xz}\rangle = -\langle p_y(6)\,|\,d_{yz}\rangle$$

$$S_{1\sigma} = \langle \sigma_y(2)\,|\,d_{x^2-y^2}\rangle = \langle \sigma_x(4)\,|\,d_{x^2-y^2}\rangle = \sqrt{3}\langle \sigma_x(1)\,|\,d_{z^2}\rangle$$
$$= \sqrt{3}\langle \sigma_y(2)\,|\,d_{z^2}\rangle = -\langle \sigma_y(5)\,|\,d_{x^2-y^2}\rangle = -\langle \sigma_x(1)\,|\,d_{x^2-y^2}\rangle$$
$$= -\sqrt{3}\langle \sigma_x(4)\,|\,d_{z^2}\rangle = -\sqrt{3}\langle (\sigma_y(5)\,|\,d_{z^2}\rangle$$

$$S_{2\sigma} = \sqrt{3}/2\langle \sigma_z(6)\,|\,d_{z^2}\rangle = -\sqrt{3}/2\langle \sigma_z(3)\,|\,d_{z^2}\rangle$$

Because of the anisotropy of the complex we have distinguished between the overlap of the orbitals of the ligands in the XY plane and that of the ligands in the Z-direction with the central atom orbital. Moreover, anisotropy of the complex introduces different mixing co-efficients λ's for different ligand orbital combinations depending upon whether the ligands lie in the XY plane or along Z-axis.

It should be noted that the expressions (1)—(5) for molecular orbitals under D_{4h} point group reduce to those of pure O_h case if

$$2\sqrt{3}\lambda_{1\sigma} = \sqrt{3}\lambda_{2\sigma} = 2\lambda_{3\sigma} = \lambda_\sigma$$
$$\lambda_{1\pi} = \lambda_{2\pi} = \lambda_{3\pi} = \lambda_\pi$$

and in pure O_h case $S_{1\pi} = S_{2\pi} = S_\pi$

and $S_{1\sigma} = S_{2\sigma} = S_\sigma$.

Covalency Reduction Factors

Covalency reduction factors for the orbital moment in the case of tetragonally distorted octahedral complex are more numerous than in the O_h case; these are given by the following quantities :

$$k_z(\pi\,\pi) = \frac{\langle \phi_{yz}\,|\,l_z\,|\,\phi_{xz}\rangle}{\langle d_{yz}\,|\,l_z\,|\,d_{xz}\rangle} \tag{14}$$

$$k_x(\pi\,\pi) = \frac{\langle \phi_{xz}\,|\,l_x\,|\,\phi_{xy}\rangle}{\langle d_{xz}\,|\,l_x\,|\,d_{xy}\rangle} = \frac{\langle \phi_{xy}\,|\,l_y\,|\,\phi_{yz}\rangle}{\langle d_{xy}\,|\,l_y\,|\,d_{yz}\rangle} = k_y(\pi\,\pi) \tag{15}$$

$$k_z(\pi\,\sigma) = \frac{\langle \phi_{xy}\,|\,l_z\,|\,\phi_{x^2-y^2}\rangle}{\langle d_{xy}\,|\,l_z\,|\,d_{x^2-y^2}\rangle} \tag{16}$$

$$k_x(\pi\,\sigma) = \frac{\langle \phi_{yz}\,|\,l_x\,|\,\phi_{x^2-y^2}\rangle}{\langle d_{yz}\,|\,l_x\,|\,d_{x^2-y^2}\rangle} = \frac{\langle \phi_{xz}\,|\,l_y\,|\,\phi_{x^2-y^2}\rangle}{\langle d_{xz}\,|\,l_y\,|\,d_{x^2-y^2}\rangle} \quad k_y(\pi\sigma) \tag{17}$$

$$k_x(\pi\sigma') \cdot \qquad \frac{\langle \phi_{xz}\,|\,l_y\,|\,\phi_{z^2}\rangle}{\langle d_{xz}\,|\,l_y\,|\,d_{z^2}\rangle} \quad k_y(\pi\sigma') \tag{18}$$

Covalency reduction factor for the spin orbit coupling co-efficient $R_i(m, n)$ where i stands for x, y and z, m stands for π and n stands for π, σ and σ' are given by similar expressions in which l_i is simply replaced by ζl_i. The expression for the reduction factors defined above, obtained after calculating the relevant matrix elements occuring in the equations (14)—(18), are given below :

$$k_z(\pi\,\pi) = 1-2\lambda^2_{1\pi}N^2_{1\pi} \quad . \quad (19)$$

$$k_x(\pi\,\pi) = k_y(\pi\,\pi) = N_{1\pi}N_{2\pi}[1-4\lambda_{3\pi}S_{1\pi}-2(\lambda_{1\pi}S_{1\pi}+\lambda_{2\pi}S_{2\pi})+2\lambda_{1\pi}\lambda_{3\pi}]. \quad . \quad (20)$$

$$k_z(\pi\sigma) = N_{2\pi}N_{2\sigma}[1-4\lambda_{3\sigma}S_{1\sigma}-4\lambda_{3\pi}S_{1\pi}-2\lambda_{3\pi}\lambda_{3p_\sigma} -2a\lambda_{3\pi}\,\lambda_{3s}\langle p_y(1)\,|\,\partial/\partial y\,|\,s(1)\rangle] \quad . \quad (21)$$

$$k_x(\pi\sigma) = k_y(\pi\sigma) = N_{1\pi}N_{2\sigma}[1-4\lambda_{3\sigma}S_{1\sigma}-2\lambda_{1\pi}S_{1\pi}-2\lambda_{2\pi}S_{2\pi} -2\lambda_{1\pi}\lambda_{3p_\sigma}-2\lambda_{1\pi}\lambda_{3s}a\langle p_z(5)\,|\,\partial/\partial z\,|\,s(5)\rangle] \quad . \quad (22)$$

$$k_x(\pi\,\sigma') = k_y(\pi\sigma') = N_{1\pi}N_{1\sigma}[1-4\sqrt{3}(\lambda_{1\sigma}S_{1\sigma}+\lambda_{2\sigma}S_{2\sigma})-2(\lambda_{1\pi}S_{1\pi}+\lambda_{1\pi}s_{2\pi}) -2/\sqrt{3}\lambda_{1\pi}\lambda_{3p_\sigma}-2/\sqrt{3}\lambda_{2\pi}\lambda_{2p_\sigma}-2/\sqrt{3}\lambda_{1\pi}\lambda_{1s}a\langle p_z(5)\,|\,\partial/\partial z\,|\,s(5) -2/\sqrt{3}\lambda_{2\pi}\lambda_{2s}\,b\langle p_y(6)\,|\,\partial/\partial y\,|\,s(6)\rangle] \quad . \quad (23)$$

Here, a and b stand for the distances of ligand lying in the XY plane and along Z direction, respectively. from the central metal atom. Since the spin orbit coupling is mainly determined by the intense field near the central nucleus,we shall assume that the matrix elements of ζl_i ($i = x, y, z$) between molecular orbital will be simply reduced in proportion to the normalization of the central ion wave functions involved :

$$R_z(\pi\,\pi) = N_{1\pi}{}^2 \quad \ldots \quad (24)$$

$$R_x(\pi\,\pi) = R_y(\pi\,\pi) = N_{1\pi}N_{2\pi} \quad \ldots \quad (25)$$

$$R_z(\pi\,\sigma) = N_{2\pi}N_{2\sigma} \quad \ldots \quad (26)$$

$$R_x(\pi\sigma) = R_y(\pi\sigma) = N_{1\pi}N_{2\sigma} \quad \ldots \quad (27)$$

$$R_x(\pi\sigma') = R_y(\pi\sigma') = N_{1\pi}N_{1\sigma} \quad \ldots \quad (28)$$

We shall apply the above expressions in two cases : (1) tetragonally distorted hexacoordinated Fe^{2+} and (2) square planar Cu^{2+} complexes. The anistropic reduction factors for orbital moment and spin orbit coupling coefficient have been obtained from the magnetic susceptibility and anisotropy experiment, and will be used to estimate the bonding parameters using the above expressions for reduction factors.

Application to Fe^{2+} complex

Magnetic susceptibility and anisotropy experiments on $Fe(NH_4SO_4)_2$, $6H_2O$ gives the following values of the reduction factors (Pal & Ghosh, in course of publication)

$$k_\parallel = k_z(\pi\,\pi) = 0.90 \qquad R_\parallel = R_z(\pi\,\pi) = 0.85$$

$$k_\perp = k_x(\pi\,\pi) = k_y(\pi\,\pi) = 0.80 \qquad R_\perp = R_x(\pi\,\pi) = R_y(\pi\,\pi) = 0.77.$$

The theoretical expressions (19) and (20) contain five independent parameters $\lambda_{1\pi}$, $\lambda_{2\pi}$, $\lambda_{3\pi}$, $S_{1\pi}$ and $S_{2\pi}$; hence these cannot be evaluated from the above four data. We therefore calculate one of the overlap integrals assuming a particular form of the radial function of the orbitals and knowing the ligand distances from X-ray data (Montgomery *et al* 1967). The three bonding parameters $\lambda_{1\pi}$, $\lambda_{2\pi}$ and $\lambda_{3\pi}$ and the other overlap integral can then be easily obtained. A self consistent test of the nature of the orbitals will then be automatically obtained if the latter overlap integral so evaluated agrees with that calculated directly. We have used the Slater orbitals for the purpose X-ray results show that the ligand O^{2-} are at 2 086Å, 2 136Å and 2 156Å, apart from the central Fe^{2+} and the bond angles slightly deviate from 90°. The overlap integral $S_{2\pi}$ corresponding to the distance 2.086Å is 0 077 as obtained from graphical interpolation of the values given in Jaffe's tables (1953). Using the experimental values of the above parameters and this value of $S_{2\pi}$ we finally get

$$\lambda_{1\pi} = 0\ 24$$
$$\lambda_{2\pi} = 0.29$$
$$\lambda_{3\pi} = 0\ 41$$
$$S_{1\pi} = 0.033$$

Jaffe's tables give the values of $S_{1\pi}$, for the ligand distances 2.156Å and 2 136Å, as 0 067 and 0 069, respectively. Considering the uniaxial approximation, the mean value of $S_{1\pi}$ is 0 068. In view of the approximations involved and lack of desired accuracy of the experimental results, the agreement is fair

Application to Cu^{2+} complex

Magnetic susceptibility and anisotropy measurements on $CuCa(CH_3COOH).6H_2O$(Biswas & Sengupta 1970) give the following values of the reduction factors :

$$k_{\|} = k_z(\pi\sigma) = 0.91 \qquad k_{\perp} = k_x(\pi\sigma) = k_y(\pi\sigma) = 0.78$$
$$R_{\|} = R_z(\pi\sigma) = 0.95 \qquad R_{\perp} = R_x(\pi\sigma) = R_y(\pi\sigma) = 0.84.$$

X-ray results (Langs & Hare, 1967) show that four oxygen atoms are coordinated to Cu^{2+} ion forming a square planar complex and each oxygen atom is about 1 97Å away from the central copper atom In the case of planar complex, the ligand nos. 3 and 6 are absent. Hence, the parameter referring to them (*i.e.* $\lambda_{2\pi}$) will not occur in the expressions (21), (22), (26) and (27). Further, following Tinkham (1956) we assume that $2p$ and $2s$ form diagonal hybrids for which $\lambda_{3\sigma} = \lambda_{3\sigma}/\sqrt{2} = \lambda_{3p_{\sigma'}}$. Hence, we have a total of five parameters as in the case of Fe^{2+} ion and these are $\lambda_{1\pi}$, $\lambda_{3\pi}$, $\lambda_{3\sigma}$ $S_{1\pi}$ and $S_{1\sigma}$. To evaluate them with the help of four experimental data ($k_{\|}$, $k_{\perp}$, $R_{\|}$, $R_{\perp}$) we follow a procedure similar to that in the case of Fe^{2+}. Using Slater value of one of the two overlap integrals $S_{1\pi}$

and $S_{1\sigma}$, we treat the other ($S_{1\pi}$ say) as one of the four unknown parameters to be evaluated from the given four experimental data and then make a consistency test of $S_{1\pi}$ so evaluated, by comparing it with the Slater value. The Slater value of $S_{1\sigma}$ is taken from Jaffe's tables remembering that $S_{1\sigma} = 1/\sqrt{2}\ (S_{1p_\sigma} + S_{1s})$ where S_{1p_σ}, S_{1s} are the overlap integrals between $d_{x^2-y^2}$ and $2p_\sigma$, $2s$ ligand orbitals, respectively. Corresponding to a distance of 1.97Å, $S_{1\sigma}$ comes out to be 0.118. Further, using Slater orbital we find that

$$a < 2p_z \mid \partial/\partial z \mid 2s > = a < 2p_y \mid \partial/\partial y \mid 2s > = \frac{Z^*}{a_0} \cdot \frac{1.97\,\text{Å}}{4\sqrt{3}} = 2.068.$$

where $Z^* = 3.85$ is the effective nuclear charge of O^{2-} $2s2p$ shell, and a is the metal-ligand distance (1.97Å). With the help of the above Slater values the four parameters $\lambda_{1\pi}$, $\lambda_{3\pi}$, $\lambda_{1\sigma}$ and $S_{1\pi}$ are then evaluated from the four experimental data using expressions (21), (22), (26) and (27). Unlike the case of Fe^{2+}, the expressions in the present case being too complicated compels us to adopt the trial and error method of evaluation of parameters instead of direct solution from the equations. The following values of the parameters give the closest fit to the above reduction factors obtained from the susceptibility and anisotropy data :

$$\lambda_{1\pi} = 0.52$$

$$\lambda_{3\sigma} = 0.01$$

$$S_{1\pi} = 0.048$$

The Slater value of $S_{1\pi}$ corresponding to a distance of 1.97Å, obtained by graphical interpolation of the values given in Jaffe's tables is 0.046. Thus, the agreement is found to be surprisingly satisfactory.

The values of the bonding parameters show that the π– bonding is unexpectedly stronger than σ bonding in the complex. Close study of the expressions (21), (22), (10), (11), (12) reveals that the large anisotropy in the reduction factors is solely due to π– bonding *i.e.*, if the π– bonding is completely neglected, the reduction factors R_t, k_t reduce to isotropic expressions which cannot be used to explain the observed anisotropy in the reduction factors. So it is evident that anisotropic reduction factors along with the anisotropic expressions derived in the present paper are very useful in determining the relative importance of σ and π bonding.

Conclusions

(1) Expressions for covalency reduction factors for orbital moment and S.O. coupling constant in a complex of D_{4h} symmetry have been derived in terms of bonding parameters and some integrals involving metal and ligand orbitals

Magnetic measurements of susceptibility and anisotropy provide the values of these reduction factors and hence a simple method to determine the bonding parameters in an anisotropic complex.

(2) The method of evaluation of bonding parameters depends on the type of radial function used to calculate some of the integrals and although lack of correct radial function suitable in the crystal is a limitation of the method, a consistency test for any assumed radial function has been indicated.

(3) In the case of O_h system, there is only one parameter of each kind π and σ. But when the system is tetragonally distorted as in the case of $Fe(NH_4)_2SO_4)_2.6H_2O$, the three π– bonding parameters assume widely different values.

(4) In the case of copper complex of D_{4h} symmetry the anisotropy in the covalency reduction factors is solely brought about by the presence of π-bonding in the system. In the square planar complex of copper calcium acetate it appears that the degree of π-admixture is very high and even surprisingly higher than the σ-admixture.

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